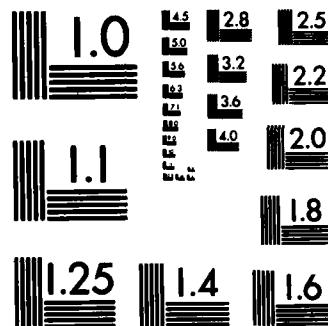END

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A121509	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
A Theory of Non-Debye Relaxation in Condensed Matter	
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
K. L. Ngai and A. K. Rajagopal	N 00014-82-K-0477

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Department of Physics and Astronomy Louisiana State University Baton Rouge, Louisiana 70803	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research Department of the Navy Rm. 582, Federal Building, 300 E. 8th St., Austin, Tx. 78701	November 15, 1982
	13. NUMBER OF PAGES
	18

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NOV 1 7 1982

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Relaxation Rates, Heat bath, time dependent transition rate.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-LF-014-6601

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A THEORY OF NON-DEBYE RELAXATION IN CONDENSED MATTER

K. L. Ngai*
Naval Research Laboratory
Washington D.C. 20375

and

A. K. Rajagopal**
Department of Physics and Astronomy
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

This paper is an expository account of a theory of relaxation phenomena in condensed matter, proposed recently by one of us (KLN). We develop in detail a picture of the relaxation process in condensed matter and show that the time dependent transition rates (TDTR) are of paramount importance in giving rise to the non-Debye relaxation. We suggest that the microscopic mechanism underlying this TDTR is another aspect of the heat bath with which the relaxing system is in contact, not considered before. The nature of the low-energy level spacings of the heat bath determine the long time relaxation process. Alternative procedures of arriving at the same TDTR are also discussed.
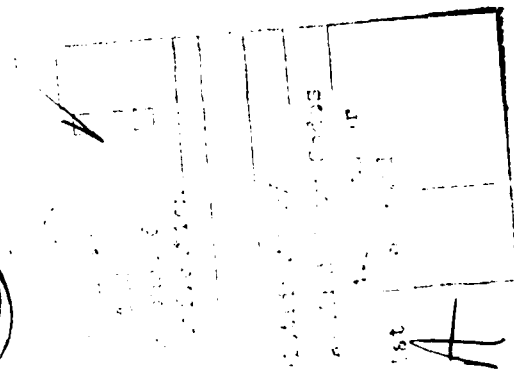
The slower than Debye relaxation in condensed matter is well-known as is evidenced by this topical meeting itself! In this paper, we develop in detail the theoretical ideas proposed earlier by one of us[1] some time ago, with the hope that some of the obscurities in that paper are removed and our current thinking on the subject is explained in some detail. Ngai[2] has given a detailed account of the experimentally observed universal form for the relaxation of any _physical_ quantity, viz.

$$\exp - a \ (t/\tau_p)^b, \quad a > 0, \ 0 < b < 1 \tag{1}$$

with τ_p, a characteristic time in the system, under diverse physical conditions. That the form, Equ.(1) is so universally found is intriguing and we seek a theoretical explanation of it which is, as far as possible, also universal and model-independent. That the relaxation be bounded by a function of the form (1) can be deduced by the mere requirement of the semiboundedness of the spectrum of the Hamiltonian describing the relaxing system and its attendant environment _and_ the square integrability of the relaxation function itself, by using the Paley-Wiener (PW) theorem, was recently proposed[3]. This observation gives rise to the Paley-Wiener criterion for relaxation which has the strong implication that indeed the usual Debye form with b=1 in Equ.(1) is ruled out because then, it would imply the spectrum of the Hamiltonian is not bounded from below, which is not physically acceptable. The aspect of square integrability of the relaxation function is new and in the absence of no information as to the nature of the long time behaviour, this requirement does not seem unpalatable. The quantum statistical evolution of a system is controlled by the Liouville operator given the initial _state_ of the system but

no other statement is made as to the nature of the time-dependence, except that for large times the system evolves into a statistical equilibrium state. No comment can be made in general as to how this state is approached with the present set up of the equations and conditions imposed. If one adds the physical requirement of the PW, then one can make detailed comments about the time dependent of approach to equilithium. This PW criterion is thus a postulate which is, as of our present understanding, a general statement, independent of the actual model. But in actual fact, the bound is attained experimentally and it is this aspect that was addressed to in Ref. 1., where it was postulated that the long-time behaviour (viz. longer than, say, 10^{-10} sec) is controlled by low energy, many-body excitations of the system with energies less than, say, 10^{+10} Hz. This leads us to the discussion of what is "relaxation" in condensed matter systems. One considers a physical property such as electric or magnetic or thermodynamic or structural etc. and examines how this property behaves as time evolves. We think of these properties as being described by the respective "species" such as dipoles for dielectric relaxations, spins for magnetic problems etc. The evolution at long times ($\gtrsim 10^{-10}$ sec) is the regime that is being considered here. This in turn implies that we are probing energy levels of the systems of order $h/10^{-10}$ sec or 10^{-1} °K. Had we considered shorter time scales such as 10^{-13} sec, the corresponding energy levels probed are of order 300°K, corresponding to excitations of the system via phonons etc. But at energies such as 10^{-1} °K, one has no known excitations and one must seek newer low energy mechanisms which drive the system to relax. Moreover, this process is necessarily "classical" involving such low energies because equilibrium thermal energies, kT, at which experiments are conducted are almost always much larger than 10^{-1} °K. We ask ourselves what these excitations could be and how can we describe

them? Ordinary quantum statistical mechanical description must accomodate these low energy processes in a crucial way in order to be able to give rise to time-dependence of relaxation of the form given by Equ.(1). From the Paley-Wiener argument, we noted earlier that the pure Debye exponential decay is not acceptable because the Hamiltonian of the system will not then be bounded from below. This difficulty is removed if we considered the coupling of the "species" to the low energy excitations of a Heat Bath in which the given system is immersed. The Heat Bath is assumed to be a larger system which is itself unaffected by the presence of the system under consideration but causes the system to relax to equilibrium which is characterized by the temperature of the heat bath. The interaction between the system and the bath is such that the relaxation comes about without anything happening to the bath itself. Conventional Hamiltonian description sets a basic energy scale and in the case of a heat bath, it can only be a continuous energy spectrum with no apparent discrete energy scale because the bath is considered very large compared to the system with which it is in contact and only the average of the bath Hamiltonian is needed to specify the temperature to which the system ultimately goes to. It therefore appears abundantly clear that the bath Hamiltonian cannot be specified in detail but yet what is needed in determining the long time relaxation phenomenon is the small energy-level spacings (of order of 10^{-4} ev or lower) of the spectrum of the heat bath.

We have thus motivated the use of a non-specific large system whose average spectral properties are only needed in developing a theory of relaxation phenomenon in condensed matter systems. We note at this stage, the description of the heat bath by the Wigner Random Matrix Hamiltonian theory seems admirably suited with our requirements stated above. We now proceed to outline our theory of relaxation. This involves three steps: (1) derivation

of the relaxation function; (2) introduction of the jump-rate of transition; and (3) the calculation of the jump-rate.

We consider some elementary entities as being the actors in the relaxation process. They flip between _equivalent energy states_ (energy degenerate) and are thought to be immersed in a bath system described by the Wigner Random Matrix Hamiltonian. We use the Gaussian Orthogonal Random Matrix Hamiltonian (GOE) because we consider the heat bath to be time-reversal invariant and also that it has a definite average energy so that one may employ a canonical ensemble picture to describe it with a fixed temperature associated with it. In equilibrium then, the actors acquire this same temperature, T.

Step 1: Derivation of the Relaxation Function

Let 1,2 represent (for simplicity we consider a two-equivalent-state system) the two equivalent system states and let $p_1(t)$ and $p_2(t)$ be their occupancies at an instant t. The interaction of these system states with the heat bath induces transitions between these two states. We are interested in computing the relaxation of this system which is merely the correlation of $P(t) \equiv p_1(t) - p_2(t)$ at two different times. We are thus interested in

$$\psi(t) \equiv - \ \langle\langle P(t_0) \ P(t_0 - t)\rangle\rangle \qquad (2)$$

$\langle\langle ---\rangle\rangle$ is the quantum statistical thermal average over the entire bath plus system hamiltonian[4]. Here t_0 is some initial time. We are interested in the long time (t → ∞) behaviour of this function. Thus, for frequencies ω<<10 Hz, which is equivalent to a temperature of 1/2 °K and below, we may make the approximation $kT \gg \hbar\omega$ and so only the classical limit of Equ.(2) suffices. In this limit, Equ.(1) becomes

$$\psi(t) = - \beta \langle P(t_0) \, \dot{P}(t_0-t) \rangle_0 \qquad (3)$$

where $\langle --- \rangle_0$ is the classical average over the equilibrium distribution function and $\beta = 1/kT$. $\dot{P}$ here denotes time derivative. It is important to stress here that in the long time limit, the classical limit of (2) suffices because $kT \gg \hbar\omega$ of the system.

Step 2: Introduction of the Jump-transition Rate

In the classical limit then, it suffices to consider a rate equation for the populations for $p_1(t)$ and $p_2(t)$ and deduce therefore a form for the relaxation function, (3). Defining $W(t)$ to be the general time-dependent jump transition rate for flipping from state 1 to 2 and vice versa, we have, the rate equations

$$\dot{p}_1(t) = - W(t) \, (p_1(t) - p_2(t))$$

$$\qquad (4)$$

$$\dot{p}_2(t) = - W(t) \, (p_2(t) - p_1(t))$$

where we have taken into account the fact that the flipping occurs between the two equivalent states only and that there is no loss of species in the process i.e., $\dot{p}_1 + \dot{p}_2 = 0$. Thus, we find at once

$$\dot{P}(t) = - 2 \, W(t) \, P(t) \qquad (5)$$

where $P(t) = p_1(t) - p_2(t)$ introduced before in Step 1. Thus, we obtain,

$$P(t) = P_0 \exp(-2 \int_0^t W(t') dt') \qquad (6)$$

where $\pm P_0$ are the values that the system takes as time progresses. And so the relaxation function, (3), has the form

$$\psi(t) = 2 \beta P_0^2 W(t) \exp \left(-2 \int_0^t W(t')dt'\right) \qquad (7)$$

It should be observed that if $W(t)$ is taken to be a constant, independent of time, say W_0, then we obtain the classical Debye result:

$$\psi(t)_{\text{Debye}} = 2 \beta P_0^2 W_0 \exp(-2 W_0 t) \qquad (8)$$

and the relaxation time is $\tau = 1/2W_0$. In obtaining the rate (or master) equation, (4), one often goes through a detailed analysis of the density matrix with Markoffian assumptions concerning the process that are going on in the system and the constant W_0 is the time-independent transition rate (TITR) given by the Golden Rule of Quantum Mechanics.[5] It should therefore be stressed that the steps I and II above are really stemming from more fundamental considerations even though we have presented them here in a simpler, physical way. The question then is to consider the evaluation of $W(t)$ in greater detail than has been done before.

Step III: Calculation of W(t)

The mechanism that gives rise to $W(t)$ is the interaction of the equivalent states introduced in Step I with low lying manybody states with energies less than say, 10^{10}Hz, in order to determine the long time decay phenomena. In doing this computation, the spontaneous emission and absorption processes are both taken into account. In fact, this calculation is very similar to the phonon side band problem except that in the present context we

have to work with the Wigner system instead of the phonons. The result is

$$W(t) = W_0 \exp(-\phi(t)) \tag{9}$$

where $\phi(t)$ is the time response of the heat bath (or Wigner system), taking care to remember that the energies involved here, $\hbar\omega$, are all much less than kT, the thermal energy, so that the associated probabilities for both emission and absorption are just constants, a factor of 1/2. Moreover, here $\phi(t)$ is real with no threshold effects.

In order to derive Equ.(9) and an explicit form for $\phi(t)$ we proceed as follows. We consider a relaxing system i.e., after a certain relaxation time τ, the system is thought to be in a relaxing state. Given such a τ, we define destruction and creation operators R and $R^\dagger$ associated with relaxation such that

$$R|> = 0 \text{ in the relaxing state} \tag{10}$$

where $|>$ refers to a pseudo "vacuum" of the relaxing state and the heat bath with which the system is in contact. Then $R^\dagger(o)|>$ is the given relaxing state at an initial reference time (this is the time the system had begun to relax!) which we denote here as the zero of our reckoning of time. We then ask how this state evolves in time. This time evolution is governed as usual by

$$R^\dagger(t)|> = e^{iHt} R^\dagger(o)e^{-iHt}|> \tag{11}$$

where H is the Hamiltonian describing the relaxing system, the heat bath with which it is in contact, and the interaction between them. This we denote by $H_0 + V$. We are thus led to the calculation of the quantity

$$b(t) = \langle| R(t)\, R^\dagger(0) |\rangle$$

$$= \langle| e^{iHt} R(o)\, e^{-iHt} R^\dagger(o) |\rangle \tag{12}$$

Since $R^\dagger(o)|\rangle$ represents the given relaxing state,

$$e^{-iHt} R^\dagger(o)|\rangle = R^\dagger(o)\; \exp{-i(H_o+V)_R t}$$

where $(H_o+V)_R$ stands for the part of the Hamiltonian associated with the relaxing state under study. Since we are here for simplicity, considering only one relaxing state, $R(o)\,R^\dagger(o) = 1$, and moreover $\langle| e^{+i(H_o+V)t} = \langle| e^{+iH_o t}$ because $\langle|$ by virtue of its definition contains no interaction between the relaxing state and the heat bath. Thus,

$$b(t) = \langle| \exp(i\,H_o t)\,(\exp -i(H_o+V)_R t)\,|\rangle \tag{13}$$

The state R in the above does not contain any index because we will invoke the "randomness" of the Heat Bath Hamiltonian to eliminate reference to any special state. With this understanding, we may drop the subscript R in Equ.(13) and compute

$$U(t) = e^{iH_o t} e^{-i(H_o+V)t} \tag{14}$$

by using standard cluster expansion techniques. The result is

$$b(t) = \exp\{\phi(t)\} \tag{15}$$

where

$$\phi(t) = \sum_{n=1}^{\infty} \phi_n(t) \tag{15a}$$

and

$$\phi_1(t) = -i \int_0^t dt_1 \, \langle |V(t_1)| \rangle \tag{15b}$$

$$\phi_2(t) = -1/2 \int_0^t dt_1 \int_0^t dt_2 \, [\langle |T(V(t_1)V(t_2)| \rangle$$

$$-\langle |V(t_1)| \rangle \, \langle |V(t_2)| \rangle] \qquad \text{etc.} \tag{15c}$$

We have thus reduced the problem to consideration of the bath states only. Remembering that the bath states are treated in a canonical ensemble framework, and since $\phi_1(t)$ involves expectation value of the interaction between the system and the bath, it may be dropped from further consideration and consider only $\phi_2(t)$. The other higher order terms may be dropped, partly because of the weak coupling between the bath and the system and partly because it would involve the multiple energy level distributions which may be expected to be of smaller significance compared to the first nontrivial contribution, ϕ_2. Thus

$$\phi_2(t) = -1/2 \sum_{\substack{i,j \\ i \neq j}} \frac{|V_{ij}|^2}{(E_i - E_j)^2} \{ \tfrac{1}{2}(1 - e^{\, it(E_i - E_j)}) + \tfrac{1}{2}(1 - e^{-\, it(E_i - E_j)}) \} \tag{16}$$

The factors $1/2$ in $\{....\}$ appear from equal occupancies of the state E_i, E_j of the bath. The sum over i,j can be written as

$$\phi_2(t) = -\sum_{\epsilon} \left(\sum_{\substack{i \neq j \\ (E_i - E_j = \epsilon)}} \tfrac{1}{2} |V_{ij}|^2 \right) \left(\frac{1 - \cos \epsilon t}{\epsilon^2} \right) \tag{17}$$

We now argue that $\tfrac{1}{2} \left(\sum_{\substack{i \neq j \\ E_i - E_j = \epsilon}} |V_{ij}|^2 \right)$ is independent of ϵ because $|V_{ij}|^2$ is

a random quantity uncorrelated with ϵ except perhaps when there are strong correlations which may occur when the energies are high such that the modes are well localized. This aspect is the basic strength of the approach of the model because the "randomness" now has been separated out of the main problem so that a universal result is obtained without the knowledge of the random distribution of $|V_{ij}|^2$ with $E_i - E_j = \epsilon$. Thus, introducing

$$\sum_{\substack{\epsilon \\ i \ne j \\ E_i - E_j = \epsilon}} (\tfrac{1}{2} \sum V_{ij}{}^2) \rightarrow \int_0^{\epsilon_c} d\epsilon \; |V|^2 \; N(\epsilon)$$

we obtain,

$$\phi_2(t) = -\int_0^{\epsilon_c} d\epsilon \; N(\epsilon) \; |V|^2 (\frac{1 - \cos \epsilon t}{\epsilon^2}) \tag{18}$$

The cut off $\epsilon_c (\approx 10^{10} Hz)$ is introduced here such that

$$|V|^2 \; N(\epsilon) = \epsilon n, \; (0 < n < 1) \tag{19}$$

is violated beyond $\epsilon = \epsilon_c$. Here we have invoked the Wigner result concerning the level-spacing distribution of a GOE. This final result then leads to the universal form[1] of relaxation given in Equ.(1) with $b = 1 - n$.

The above arguments are at a physical level, lacking perhaps the rigor of mathematics. Our aim was to give a simple physical derivation of Equ.(1). There is a completely heuristic, mathematical way of arriving at such a result also by invoking the mathematical idea of "fractional Brownian Motion" (and the fractal times) of Mandelbrot and van Ness[7]. This procedure would imply

that relaxation process may be thought of as basically a generalized diffusion process. The conventional diffusion process using a Langevin equation with white noise stochastic process leads to the Debye exponential relaxation. If one believes in the diffusion mechanism as underlying relaxation processes, then one is forced to modify the white noise stochastic picture of diffusion by the "fractional Brownian noise" so that one obtains a non-Debye relaxation of the form given by Equ.(1). But we know[2] that not all physical relaxation processes can be related to Brownian motion and so this model suffers from a lack of physical basis in spite of the fact that one may be able derive non-exponential decay of the form given by Equ.(1). This is an interesting mathematical aspect of the non-Debye relaxation. A purist may object to this approach to relaxation because the basic premise here is that the underlying rate equation is a Langevin type equation with fractional brownian noise, to which one has no answer except to say that it seems to lead us to the observed result. There are attendant changes in the Einstein relation etc. that ensue such a framework and the reader may refer to Ref. 8 for a discussion of it.

There is another level at which the present problem may be attacked. This is perhaps the most complete theory but even here certain characteristics of the heat bath have to be introduced at a particular point. We present this approach for the complete non-believer with the hope that this approach may be appealing to both physically and mathematically minded person. In this approach one begins with a density matrix for a system, heat bath, and their mutual interaction with the explicit knowledge that the heat bath is much larger than the system in contact with it and their mutual interaction is weak such that the leading order calculation suffices. Moreover one constructs the system density matrix by taking a trace over the bath so that the result is free of all bath variables. The difference between this approach and a

similar approach found in the literature[5] in the derivation of the master equation for the system density matrix is that in our procedure, while we make the Markoff approximation, we keep the time-dependence of the transition rate. By so doing, we bring in details of the bath Hamiltonian. Also, invoking the Wigner's random matrix Hamiltonian as a description of the heat bath, which seems most appropriate for describing the unknown, large system, we see that this program makes the derivation of an equation such as Equ.(5) including an expression for W(t) quite acceptable, on a formal level.

In this case, we do not invoke the PW theorem but we are in comformity with it. We use the known information about the system plus heat bath at the initial time where it is given that the bath is in a canonical ensemble and the system is in some preassigned system density matrix and the above program answers the question of ultimate time evolution of the system to an equilibrium ensemble state. In so doing, unlike in the equilibrium statistical mechanical theory where the system relaxes to an equilibrium state with the same temperature as the heat bath, which is merely the average of the heat bath hamiltonian, the long time relaxation behaviour depends on the nature of the bath spectrum for small energy level spacings. Using the results of the Gaussian Orthogonal ensemble theory of random matrix Hamiltonian as was done in Ref. 1, we deduce the universal relaxation of the form given of Equ.(1). For a discussion of this theory but in the context of quantum mechanics of the system plus bath system, one may refer to the paper of Rajagopal and Wiegel.[9]

In the derivation of the universal relaxation function, Eq.(1) given earlier, the bath states take a subservient role. The relaxation species is the center of attention. Its relaxation rate is calculated and the bath states come into the picture only in how they modify its relaxation rate.

Stimulated by an idea of Palmer and Anderson[10], we shall give here another derivation of the universal law (1) while treating both the relaxation species and the bath states altogether on an equal footing. That is, we start by writing down the relaxation rate as[11]

$$W(t) = W_0 e^{-(E - T \Delta S)/kT} \tag{20}$$

Here $W_0 \exp(-E/kT)$ represents the transition rate of the relaxation species if its interaction with the bath states is ignored. Thus E is an activation energy if its value is nonzero. W_0 is the "attempt frequency" of the primary species. The quantity ΔS is the entropy of the bath states measured from its maximum value. Initially before the commencement of relaxation, the bath states are in equilbrium and its entropy must have a maximum value, S_{max}.

After relaxation has commenced at t=0, the interaction between the relaxing species and the bath states causes excitation and deexcitation of the bath. We calculate the probability that the bath remains in the same state after the interaction V is turned on, in the lowest order perturbation theory. This probability is

$$p_i = 1 - \frac{1}{2} \sum_{j (\neq i)} |V_{ij}|^2 \frac{(1 - \cos(E_i - E_j)t)}{(E_i - E_j)^2} \tag{21}$$

because we assume that the bath states are perturbed very little by the interaction with the system. If the interaction V were neglected, $p_i = 1$ as it should, by construction. Then, calculating the entropy change due to this, we have, to leading order in the interaction,

$$\frac{\Delta S}{k} = \sum_i P_i \ln p_i \simeq -\frac{1}{2} \sum_i \sum_{j \neq i} |V_{ij}|^2 \quad \frac{\{1-\cos(E_i-E_j)t]}{(E_i-E_j)^2} \tag{22}$$

In the above, i,j refer to a group of states of the bath which form the bath ensemble.

Following the same arguments as before, (see Equ. 17,18,19) we find

$$\frac{\Delta S}{k} = -n \ln \epsilon_c t + \frac{\Delta S}{k} \tag{23}$$

where $\Delta S_>$ is the contribution to the entropy change arising from the states above ϵ_c and any other mechanism and will depend on temperature etc. in general especially near a glass transition, for example. Substitution of Equ.(23) into Equ.(20) leads immediately to the TDTR

$$W(t) = (\epsilon_c t)^{-n} W_0 e^{-E/kT} e^{\Delta S_>/k} \tag{24}$$

This is turn leads to the universal relaxation function

$$\exp \{-t^{1-n} \epsilon_c^{-n} W_0^{-1} \exp(E/kT - \Delta S_>/k)\} \tag{25}$$

$$\equiv \exp - (t/\tau_p)^{1-n} \tag{26}$$

and the renormalization relation

$$\tau_p = \tau_0^{1/1-n} \tag{27}$$

between the observed τ_p and the microscopic $\tau_o = (W_o^{-1} \exp(\frac{E}{kT} - \frac{\Delta S}{k}))$.

Obviously the present approach and the earlier one are closely related. Both have the infrared divergent bath states excitation at their root. The difference between the earlier approach and the present one is that the entire system, relaxation species plus the bath states are considered at the same time. It is not surprising that we obtain the same results independent of the approach. However the present approach which lets its bath states play a more active role enables further interpretation of the physical processes that occur in relaxation phenomena in condensed matter. Relaxation of the species will lead to an increase in entropy with time as all irreversible processes do according to the second law of thermodynamics. What is interesting here is that not only the relaxation is non-exponential in time and have the universal form of Eq.(1), but also this relaxation is accompanied by a decrease in entropy of the bath states.

In closing we would like to discuss another derivation of the universal relaxation function which is totally different in spirit from the mechanistic models given earlier. Given the universal form of the macroscopic relaxation function in Eq.(1), one is led to consider a microscopic mechanism underlying relaxation phenomenon in general. We may think of the relaxing body as being composed of some species of relaxing entities such as electric dipoles in a dielectric, charge carriers in a semiconductor, etc., each of which had identically distributed energy variables with the same energy distribution. The macroscopic energy distribution function $\rho(\epsilon)$ associated with the relaxing body for low energies is the limit distribution of normalized sums of the microscopic energy variables. A similar procedure is involved in statistical mechanics for deriving equilibrium ensemble distributions. The resulting macroscopic density distribution $\rho(\epsilon)$ necessarily obeys the

relationship[12]

$$\rho(a\epsilon+b) = (a_1a_2/a) \int_{-\infty}^{\infty} d\epsilon'\rho(a_1(\epsilon-\epsilon')+b_1)\rho(a_2\epsilon'+b_2) \tag{2}$$

for every set of parameters $a_i > 0$, b_i with the corresponding $a > 0$, b related to the parameters a_i, b_i. The relaxation function is proportional to the modulus square of the Fourier transform, $|c(t)|^2$, of the energy distribution function $\rho(\epsilon)$. For distributions obeying Eq. (2) this is necessarily of the form[12]

$$|c(t)|^2 = e^{-a|t|^b}, \quad a>0, \quad 0<b<2 \tag{3}$$

If in addition, the spectrum of the Hamiltonian is semibounded, then the Paley-Wiener theorem applies and the values of b would have to be in the smaller range $0<b<1$, leading us again to Eq.(1). For such microscopic models, we see that the Paley-Wiener bound becomes exact.

We have thus given here a variety of general arguments at different levels to obtain the non-Debye relaxation in condensed matter properties.

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